

1.044.503



# PATENT SPECIFICATION

NO DRAWINGS

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## COMPLETE SPECIFICATION

### Cold-Worked Polyolefin Compositions

We, W. R. GRACE & Co., a Corporation organized and existing under the laws of the State of Connecticut, United States of America, of 7, Hanover Square, New York 5, New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the cold-working of filled polyolefin compositions, and is an improvement in or modification of the invention disclosed in our Specification No. 29386/63.

The use of inorganic fillers as extenders and/or reinforcing agents for rubbers and some other resins is well established. Most attempts to use fillers in a similar manner to extend and/or reinforce the more crystalline polyolefins, however, have met with failure, brittle products generally being obtained, even with moderate filler concentrations. Previous attempts have been made to produce poly (*alpha*-olefins) filler blends using conventional inert fillers alone, and although occasionally these blends are found to have greater tensile strength than the unfilled polymer, most of them are too brittle to be useful as general purpose resin-base compositions. On the whole, reported studies of poly (*alpha*-olefin) filler blends indicate that satisfactory products are rarely obtained. Small amounts of some inorganic materials can be blended into poly (*alpha*-olefins) as pigments, but in amounts too small to serve other purposes.

Fillers are now widely used as extenders for glass fibre reinforced resins. In most cases of this type, the filler does not impart any reinforcement, but does have a favourable effect on cost, shrinkage, thermal effects, surface properties, and flow properties. However, apparently no other material is reinforced by

fillers to the same extent as the natural or synthetic rubbers.

In Specification No. 29386/63 (Serial No. 1,044,028) we have disclosed polyolefin compositions which unexpectedly retain a substantial proportion of the flexibility, impact resistance and strength of the base polymers, said compositions comprising a three component system consisting of (i) a polyolefin of molecular weight sufficiently high to give it a standard load melt index of substantially zero (ii) an inert filler material, and (iii) plasticiser. We have also disclosed that the compositions can be processed by extrusion, injection moulding, vacuum forming, or calendering, and that cold pressing produces changes in properties that are desirable under some circumstances. A wide variety of articles such as films, sheets and other shaped articles can be produced from the blends, and the articles can be rendered porous, if desired, by removing part or all of the filler, plasticiser or both by solvent extraction, using either aqueous or organic solvents, depending on the particular fillers and plasticisers used.

Such blends have a wide variety of uses and are particularly advantageous because of their relatively low cost. Compositions having a high concentration of filler are particularly interesting because of the low cost of fillers and their ability to counteract the tendency (if any) for plasticiser exudation to occur. While both the relatively lowly filled blends and highly filled blends are sufficiently flexible for many uses, even greater flexibility would be desirable, particularly for the highly filled blends.

According to the present invention, a homogeneous blend comprising 10—80% by volume of a crystalline poly (*alpha*-olefin) having a standard load melt index as specified in ASTM D 1238—52T of substantially zero, the *alpha*-olefin having from 2—4 carbons, 5—

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- 60% by volume of inert particulate filler material and 15—85% by volume of plasticiser, which is defined as a material that lowers the melt viscosity, improves the flexibility of the final composition and aids the production of porous objects, is subjected to cold working, i.e. mechanical deformation under pressure at a temperature below the softening point of the blend (i.e. below the maximum temperature at which deformation produces crystalline orientation in the polymer), for the thickness of at least a portion of the blend to be decreased by at least 1%, preferably at least 5%.
- We have found that by this means the blends are rendered more flexible. Furthermore, we have found with decreases in thickness of at least 20% the rate of plasticiser exudation is decreased.
- The blend is desirably first shaped into a form which is suitable for the cold working operation. The cold working may be carried out, for example, by pressing, stamping, compression moulding, embossing or calendar rolling (at a temperature below the softening point of the blend). Thus, if, for example, calendaring is to be used to cold work the blend, the blend may first be shaped into a "sheet." (As used herein the term "sheet" includes a slab, film, tape or ribbon). Any sheet forming operation that is suitable for treating the blend above its softening point may be used, for example compression moulding, injection moulding or extrusion. The composition is generally introduced into the processing equipment in the form of pellets. The particular process temperatures and other conditions which provide the optimum results differ somewhat from blend to blend, but determination of such factors is a matter of mere routine. The thus-formed sheet is cooled below its softening temperature before being cold worked.
- The invention therefore also comprises a method of treating the blends comprising forming the blend into a sheet (as hereinbefore defined) at a temperature above the coalescing temperature of the blend, cooling the sheet below the softening temperature of the blend, and deforming the cooled sheet by applying pressure, e.g. using a press or roll, against at least a portion of the surface of the sheet, which pressure is sufficient to decrease the thickness of at least a portion of the sheet by at least 1% preferably at least 5%, and by at least 20% if it is desired to reduce plasticiser exudation rates.
- The cold working operation may be carried out at any temperature below the softening point of the blends. Working temperatures which are 10°F. below the softening point are suitable but ambient temperatures are preferred for convenience, ease of control, and economy.
- The cold worked blends can be made porous by extraction of part or all of the filler, plasticiser or both in the way disclosed for the compositions generally in Specification No. 29,386/63 (Serial No. 1,044,028). It has also been found that blends from which the plasticiser had been extracted were also made more flexible by cold working.
- The poly (*alpha*-olefin) component may comprise one or more of the following crystalline polyolefins: high density polyethylene, low density polyethylene, polypropylene, ethylene-butene copolymer, poly (butene-1), propylene-(butene-1) copolymer and ethylene-propylene copolymer.
- Preferred water-insoluble fillers include kaolin, calcium silicate, calcium carbonate, magnesium carbonate, magnesium oxide, stannic oxide, mica, glass beads, glass flakes, asbestos, carbon black, silica, aluminium polysilicate, montmorillonite, attapulgite, talc, wood flock, and mixtures thereof. However, any finely divided material which retains its particulate characteristics under the processing conditions may be suitable and the following classes of compounds may be cited by way of example.
- (a) Carbon blacks, coal dust, graphite.
  - (b) Metal oxides and hydroxides, especially those of silicon, aluminium, calcium, magnesium, barium, titanium, iron, zinc, tin,
  - (c) Metal carbonates, especially those of calcium, magnesium, sodium, sodium, and potassium,
  - (d) Metal silicates and aluminates; naturally occurring clays such as montmorillonite, kaolin, attapulgite, asbestos, mica, muscovite, talc, vermiculite; precipitated silicates, synthetic and natural zeolites, portland cement, calcium silicate, aluminium polysilicate, alumina silica gels,
  - (e) Metals such as aluminium, lead,
  - (f) Polymers such as nylon and phenol formaldehyde resins,
  - (g) Wood flour, fibres and bark products,
  - (h) Glass particles such as microbeads, hollow microspheres, flake, fibre,
  - (i) Molybdenum disulphide, and zinc sulphide.
- Preferred water-soluble fillers include sodium chloride, potassium chloride, calcium chloride, sodium acetate, potassium acetate, calcium acetate, copper acetate, barium acetate, sodium sulphate, potassium sulphate, sodium phosphate, potassium phosphate, sodium nitrate, potassium nitrate, sugar, and mixtures thereof.
- Preferred water-insoluble plasticisers include petroleum oils, petroleum waxes, butyl stearate, dibutyl sebacate, dioctyl sebacate, ethylene-vinyl acetate copolymer, polyisobutylene, diisodecyl phthalate, dioctyl fumarate, asphalt, polyester-glycol, octyl epoxy tallate, chlorinated biphenyl and mixtures thereof. The following illustrative types of compounds are also suitable:
- (a) Esters, e.g. sebacates, fumarates, phthalates, stearates, adipates, citrates, etc.; epoxy compounds; polyesters.

- (b) Phosphate esters.
- (c) Hydrocarbons-petroleum oils, waxes, resins, asphalt and those materials containing oxygen, nitrogen, and sulphur groups, blown asphalt; pure compounds such as eicosane, low molecular weight polymers such as polyisobutylene, polybutadiene, hydrocarbon resins, polystyrene and homologue copolymers of styrene, poly (*alpha*-methyl styrene), atactic polypropylene, ethylene-propylene copolymer, ethylene-vinyl acetate copolymer, oxidized polyethylene, coumarone-indene resins, terpene resins, etc.
- (d) Chlorinated hydrocarbons including oils and waxes.
- (e) Sulphonamide, coumarone indene, laurone, tall oil, drying oils such as linseed oil.
- Preferred water-soluble plasticisers include glycol, glycol ethers and esters, glycerin, glycerol monoacetate, diethylene glycol, diethylene glycol ethers and esters, triethylene glycol, polyethylene glycol (molecular weight of about 400—20,000), propylene glycol, diisopropylene glycol, polypropylene glycol (molecular weight of about 260—1200), trimethylene glycol, tetramethylene glycol, 2,3-butylene glycol, triethyl phosphate, polyvinyl alcohol, partially hydrolized polyvinyl acetate, polyacrylic acid, polyvinyl pyrrolidone and mixtures thereof.
- The general considerations affecting the choice and use of the plasticisers and fillers are discussed in Specification No. 29,386/63 (Serial No. 1,044,028). It is particularly to be noted, however, that all combinations of water-soluble and water-insoluble fillers and plasticisers may be used, and that part or all of the filler, plasticiser or both may be removed by solvent extraction.
- It is also to be noted that up to 85% by volume of the polyethylene, or other polyolefin of melt index substantially zero may be replaced by polyethylene, for example, having a melt index of 0.1 or greater.
- A particularly suitable composition is a homogeneous blend of a poly (alpha-olefin) having a standard load melt of substantially zero containing 30—75 percent by volume of plasticiser and 10—55 percent by volume of filler.
- The effects of cold working in accordance with the invention upon the strength and flexibility characteristics of representative blends is shown in Tables I and II.
- The significance of the various designations for the polymer, filler and plasticiser are as follows:
- Grex—4: A particle formed polyethylene sold by W. R. Grace & Co., under the designation FF—60—018 having a S.L.M.I. of 0.0 and a H.L.M.I. (High Load Melt Index) of 1.8, a specific gravity of 0.945 and RSV (Reduced Standard Viscosity) of 4.5.
- Fldpe\* A fractional low density polyethylene manufactured by W. R. Grace & Co., having a S.L.M.I. of 0.8 and a H.L.M.I. of 0.93.
- \* High molecular weight fraction of low density polyethylene obtained by solvent extraction.

TABLE I  
Physical Properties of Cold Worked Blends

| Sample No.       | Composition, % by Volume |        |             | Type of Cold Working | Tensile Modulus psi. | Stress at Yield Point, psi. | Elongation at Yield Point, % | Tensile Strength psi. | Elongation At Failure % |      |       |     |
|------------------|--------------------------|--------|-------------|----------------------|----------------------|-----------------------------|------------------------------|-----------------------|-------------------------|------|-------|-----|
|                  | Polymer                  | Filler | Plasticiser |                      |                      |                             |                              |                       |                         |      |       |     |
| 1                | GreX-4                   | 50     | H121        | 30                   | SF412                | 20                          | CP <sup>(1)</sup>            | 55,000                | 890                     | 31.2 | 710   | 470 |
| 2                | GreX-4                   | 40     | H121        | 40                   | SF412                | 20                          | CP                           | 20,000                | 670                     | 195  | 640   | 290 |
| 3                | GreX-4                   | 20     | H121        | 40                   | SF412                | 40                          | None                         | 74,000                | 750                     | 9.6  | 710   | 23  |
| 4                | GreX-4                   | 20     | H121        | 40                   | SF412                | 40                          | CR <sup>(2)</sup>            | 38,000                | 1,280                   | 50   | 1,330 | 180 |
| 5 <sup>(3)</sup> | GreX-4                   | 20     | H121        | 40                   | 0                    | 0                           | CR                           | 79,000                | 1,330                   | 71.5 | 1,320 | 90  |
| 6 <sup>(4)</sup> | GreX-4                   | 20     | H121        | 40                   | 0                    | 0                           | CR                           | 380,000               | 1,830                   | 4.3  | 1,730 | 41  |
| 7 <sup>(5)</sup> | GreX-4                   | 20     | H121        | 40                   | 0                    | 0                           | None                         | 108,000               | 800                     | 7.6  | 830   | 60  |
| 8                | GreX-4                   | 40     | H121        | 45                   | SF412                | 15                          | None                         | 335,000               | 2,870                   | 5.6  | 2,350 | 49  |
| 9                | GreX-4                   | 40     | H121        | 45                   | SF412                | 15                          | CR                           | 193,000               | 3,230                   | 35.3 | 3,240 | 76  |
| 10               | GreX-4                   | 40     | H121        | 30                   | SWX                  | 30                          | None                         | 221,000               | 2,030                   | 10.1 | 1,910 | 15  |
| 11               | GreX-4                   | 40     | H121        | 30                   | SWX                  | 30                          | CR                           | 146,000               | 2,150                   | 21.9 | 1,610 | 217 |
| 12               | GreX-4                   | 25     | H121        | 35                   | SF412                | 40                          | CP                           | 68,000                | 820                     | 10.2 | 750   | 95  |
| 13               | GreX-4                   | 25     | H121        | 35                   | SF412                | 40                          | CR                           | 38,000                | 1,280                   | 50.0 | 1,330 | 180 |

- (<sup>1</sup>) Cold pressed at room temperature for 10 minutes.  
(<sup>2</sup>) Cold rolling at room temperature at pressures of about 2000—3000 psi.  
(<sup>3</sup>) Sample 3 which was extracted after cold rolling.  
(<sup>4</sup>) Sample 3 which was cold rolled after extraction.  
(<sup>5</sup>) Sample 3 which was extracted without cold working.

TABLE II  
Physical Properties of Cold Rolled Blends

| Sample No. | Composition, % by Volume |         |             | Sample      | Tensile Modulus psi. | Tensile Strength psi. | Elongation at Failure, % |
|------------|--------------------------|---------|-------------|-------------|----------------------|-----------------------|--------------------------|
|            | Polymer                  | Filler  | Plasticiser |             |                      |                       |                          |
| 14         | FlDpe                    | H121 30 | SF412 30    | Control     | 20,000               | 735                   | 52                       |
| 15         | FlDpe                    | H121 30 | SF412 30    | Cold-rolled | 13,000               | 940                   | 73                       |
| 16         | GreX-7                   | H121 30 | SF412 30    | Control     | 53,000               | 1,250                 | 30                       |
| 17         | GreX-7 40                | H121 30 | SF412 30    | Cold-rolled | 40,000               | 1,430                 | 85                       |
| 18         | GreX-7 30                | H121 40 | SF412 30    | Control     | 103,000              | 1,150                 | 42                       |
| 19         | GreX-7 30                | H121 40 | SF412 30    | Cold-rolled | 49,000               | 1,520                 | 67                       |
| 20         | GreX-7 60                | H121 20 | SF412 20    | Control     | 132,000              | 2,431                 | 24                       |
| 21         | GreX-7 60                | H121 20 | SF412 20    | Cold-rolled | 115,000              | 3,460                 | 172                      |
| 22         | GreX-7 25                | H121 30 | SF412 45    | Control     | 17,000               | 660                   | 57                       |
| 23         | GreX-7 25                | H121 30 | SF412 45    | Cold-rolled | 13,000               | 860                   | 64                       |

GreX-7: A polypropylene sold by W. R. Grace & Co., under the designation 9000G having a S.L.M.I. of 0.0, a H.L.M.I. of 0.03 and RSV of 20.

H121: An aluminium silicate (kaolinite) sold by Georgia Kaolin Co., under the name Hydrite 121 and of average particle size 1.5 microns.

SF412: A plasticiser sold by Shell Oil Co. under the name Shellflex 412 comprising 50% paraffinic carbon, 43% naphthenic carbon and 7% aromatic carbon, and having a viscosity of 559 Seconds, Saybolt Universal at 100°F. and 56 Seconds, Saybolt Universal at 210°F.

SWX: A petroleum wax sold by Shell Oil Co., under the designation Shellwax 90 and having a viscosity of 81 Seconds, Saybolt Universal at 210°F.

- As can be seen from Table I and Table II, the tensile modulus of the blends is lowered while the elongation at yield point, an indication of the flexibility, is greatly increased.
- 5 Apparently, some reduction of the crystallinity of the poly (*alpha*-olefin) is produced by the cold working. Similiar results occur with the other blends disclosed.
- The relationship between the degree of cold rolling as measured by the percentage reduction in sheet thickness and the physical properties of the cold rolled sheet is shown in Table III.
- HR, referred to in Table III, is an aluminium silicate (kaolinite) sold by the Georgia Kaolin Co. under the name Hydrite R having an average particle size of 0.77 microns.

TABLE III

Physical Properties<sup>(1)</sup> of Cold-Rolled Blends<sup>(2)</sup>

| Sample No. | Sheet Thickness Reduction by Cold Rolling, % | Tensile Modulus psi. | Stress at Yield Point psi. | Elongation at Yield % | Tensile Stress psi. | Elongation at Failure |
|------------|--|----------------------|----------------------------|-----------------------|---------------------|-----------------------|
| 24         | 0  | 60,000               | 930                        | 20.7                  | 900                 | 790                   |
| 25         | 9  | 44,000               | 1000                       | 17.8                  | 980                 | 710                   |
| 26         | 22   | 35,000               | 1030                       | 33.7                  | 1260                | 700                   |
| 27         | 42   | 47,000               | 1260                       | 70.9                  | 1840                | 580                   |
| 28         | 55   | 41,000               | ( <sup>3</sup> )           | ( <sup>3</sup> )      | 220                 | 470                   |
| 29         | 61   | 43,000               | ( <sup>3</sup> )           | ( <sup>3</sup> )      | 2700                | 420                   |

<sup>(1)</sup> Tests made in machine direction of sheets, direction of rolling.<sup>(2)</sup> Blend consisting of 30% Grex-4, 30% HR, and 40% SF412.<sup>(3)</sup> Blend did not exhibit a yield point.

- As can be seen from the results shown in Table III, any degree of cold working increases flexibility of the blend, and greater amounts of cold working produce greater increases in flexibility. Similar results occur with the other blends disclosed.
- Plasticiser exudation rates of compositions that have been cold worked in accordance with this invention are shown in Table IV and Table V.
- EFT referred to in Table V is a carbon black sold by Cabot Corp. under the name Eltex.

TABLE IV

Oil Exudation from Cold Worked Blends<sup>(1)</sup>

| Sample No. | Thickness Reduction % | Weight loss %, at 100°C. |       |       |
|------------|-----------------------|--------------------------|-------|-------|
|            |                       | 1 Hr.                    | 4 Hr. | 6 Hr. |
| 30         | 0                     | 0.80                     | 1.29  | 1.44  |
| 31         | 6.25                  | 1.22                     | 1.67  |       |
| 32         | 9.2                   | 1.31                     | 1.68  |       |
| 33         | 10.4                  | 1.39                     | 1.84  |       |
| 34         | 12.0                  | 1.52                     | 1.88  |       |
| 35         | 12.7                  | 1.34                     | 1.72  |       |
| 36         | 15.0                  | 1.38                     | 1.54  |       |
| 37         | 16.0                  | 1.43                     | 1.81  | 1.91  |
| 38         | 16.2                  | 1.21                     | 1.63  |       |
| 39         | 17.2                  | 1.30                     | 1.65  |       |
| 40         | 17.5                  | 1.51                     | 1.93  |       |
| 41         | 19.5                  | 1.23                     | 1.66  |       |
| 42         | 20.9                  | 0.91                     | 1.36  |       |
| 43         | 22.6                  | 0.64                     | 1.01  |       |
| 44         | 23.5                  | 0.89                     | 1.28  |       |
| 45         | 25.8                  | 0.37                     | 0.81  |       |
| 46         | 31.0                  | 0.08                     | 0.49  | 0.66  |
| 47         | 38.0                  | -0.38 <sup>(2)</sup>     | -0.11 | 0.02  |
| 48         | 45.0                  | 0.13                     | 0.50  | 0.71  |

<sup>(1)</sup> Cold rolled at ambient temperature, composition was 30% Grex-4, 30% HR and 40% SF412, by volume.

<sup>(2)</sup> Weight gain after aging at ambient temperature due to moisture adsorption by filler.



TABLE V  
Oil Exudation Rates from Cold Worked Blends<sup>(1)</sup>

| Sample No. | Composition       | Thickness Reduction % | Weight loss % at 100°F. |       |         |
|------------|-------------------|-----------------------|-------------------------|-------|---------|
|            |                   |                       | 0.5 Hr.                 | 1 Hr. | 2.5 Hr. |
| 49         | C <sup>(2)</sup>  | 0                     | 0.70                    |       | 1.0     |
| 50         | C                 | 16                    | 1.33                    |       | 1.7     |
| 51         | C                 | 33                    | 0.22                    |       | 0.3     |
| 52         | C                 | 39                    | 0.09                    |       | 0.3     |
| 53         | C                 | 51                    | 0.23                    |       | 0.5     |
| 54         | C                 | 61                    | 0.42                    |       | 0.8     |
| 55         | D1 <sup>(3)</sup> | 0                     | 0.45                    | 0.62  | 0.74    |
| 56         | D1                | 9                     | 1.02                    | 1.24  | 1.36    |
| 57         | D1                | 35                    | 0.00                    | 0.02  | 0.10    |
| 58         | D2 <sup>(4)</sup> | 0                     | 0.48                    | 0.55  | 0.74    |
| 59         | D2                | 9                     | 1.21                    | 1.30  | 1.45    |
| 60         | D2                | 33                    | 0.12                    | 0.16  | 0.25    |

<sup>(1)</sup> Cold rolled at ambient temperature.  
<sup>(2)</sup> 30% Grex-4, 25% HR, 5% EFT, 40 % SF412.  
<sup>(3)</sup> 30% Grex-4, 30% BaSO<sub>3</sub>, 40% SF412; original sheet thickness was 0.098 cm.  
<sup>(4)</sup> Composition of <sup>(3)</sup>, original sheet thickness was 0.044 cm.

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The weight loss measured at 100°C. is due to two factors. All samples are wiped dry after the heat treatment and before cooling, and then the sample is weighed. Exuded oil is removed by the wiping, and the weight loss reflects the extent of the exudation. The surface of samples which had received no cold working or only slightly cold working were wetted with plasticiser shortly after being heated. With progressively greater cold working, as represented by the decrease in thickness after cold rolling, the samples remained progressively drier when heated. Wiping removed the plasticiser wetting the sample surface.

However, especially with the thinner samples, a steady weight loss upon heating was observed. This latter type of weight loss is due to volatilization of the plasticiser and volatile materials absorbed on the filler and is determined by diffusion rates in the sample.

As clearly illustrated by the weight loss measurements, exudation rates are not reduced but, on the contrary, are increased by deformations of the sheet materials up to about 12.5 percent deformation. Above this critical point, exudation rates suddenly decrease. Similar tests made with the other poly (alpha-olefins), fillers and plasticisers disclosed exhibited the same results. Apparently when a deformation greater than about 12.5 percent is applied, some physical effect occurs which increases the plasticiser retention capabilities of the blend. It is thought that void spaces around the filler might be produced which would increase the adsorption characteristics of the filler but we do not intend that this invention be limited in any way by this theory. A deformation greater than 20 percent is necessary to decrease the oil exudation characteristic of the blends.

The cold worked products of this invention are useful as tape backings, pipe wrappings,

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- heavy duty film, and other conventional uses of flexible plastic films. The more flexible cold worked blends which have been rendered porous by extraction of the plasticiser and/or the filler are sufficiently pliable to be used as a synthetic leather substitute. Because of the decreased plasticiser exudation, the cold worked blends have increased utility where such exudation would be undesirable and especially in elevated temperature environments.
- WHAT WE CLAIM IS:—
1. A method of treating a homogeneous blend comprising 10—80% by volume of a crystalline poly (*alpha*-olefin) having a standard load melt index of substantially zero, the *alpha*-olefin having from 2—4 carbon atoms, 5—60% by volume of inert particulate filler material, and 15—85% by volume of plasticiser as hereinbefore defined, which method comprises subjecting the blend to sufficient cold working (as hereinbefore defined) that the thickness of at least a portion of the blend is decreased by at least 1%.
  2. A method of treating a homogeneous blend specified in claim 1 which comprises forming the blend in to a sheet (as hereinbefore defined) at a temperature above the coalescing temperature of the blend, cooling the sheet below the softening temperature of the blend, and deforming the cooled sheet by applying pressure against at least a portion of the surface of the sheet, which pressure is sufficient to decrease the thickness of at least a portion of the sheet by at least 1%.
  3. A method according to claim 1 or 2, wherein the pressure is applied by means of a press.
  4. A method according to claim 1 or 2, wherein the pressure is applied by means of a roll.
  5. A method according to claim 1 or 2, wherein the pressure is applied by pressing, stamping, compression moulding or calender rolling.
  6. A method according to any one of the preceding claims, wherein the thickness is decreased by at least 5%.
  7. A method according to any one of the preceding claims, wherein the thickness is decreased by at least 20%.
  8. A method according to any one of the preceding claims, wherein the poly (*alpha*-olefin) component comprises one or more of the following crystalline polyolefins: high density polyethylene, low density polyethylene, polypropylene and ethylene-butene copolymer.
  9. A method according to any one of the preceding claims, wherein the blend contains one or more of the following water-insoluble fillers: kaolin, calcium silicate, calcium carbonate, magnesium carbonate, magnesium oxide, stannic oxide, mica, glass beads, glass flakes, asbestos, carbon black, silica, aluminium polysilicate, montmorillonite, attapulgite, talc and wood flock.
  10. A method according to any one of the preceding claims, wherein the blend contains one or more of the following water-soluble fillers: sodium chloride, potassium chloride, calcium chloride, sodium acetate, potassium acetate, calcium acetate, copper acetate, barium acetate, sodium sulphate, potassium sulphate, sodium phosphate, potassium phosphate, sodium nitrate, potassium nitrate and sugar.
  11. A method according to any one of the preceding claims, wherein the blend contains one or more of the following water-insoluble plasticisers: petroleum oils, petroleum waxes, butyl stearate, dibutyl sebacate, dioctyl sebacate, ethylene-vinyl acetate copolymer, polyisobutylene, diisodecyl phthalate, dioctyl fumarate, asphalt, polyester glycol, octyl epoxy tallate, and chlorinated biphenyl.
  12. A method according to any one of the preceding claims, wherein the blend contains one or more of the following water-soluble plasticisers: glycol, a glycol ether or ester, glycerin, glycerol monoacetate, diethylene glycol, a diethylene glycol ether or ester, triethylene glycol, polyethylene glycol (molecular weight of about 400—20,000), propylene glycol, diisopropylene glycol, polypropylene glycol (molecular weight of about 260—1200), trimethylene glycol, tetramethylene glycol, 2,3-butylene glycol, triethyl phosphate, polyvinyl alcohol, partially hydrolyzed polyvinyl acetate, polyacrylic acid, and polyvinyl pyrrolidone.
  13. A method according to any one of the preceding claims, wherein the homogeneous blend of the poly(*alpha*-olefin) contains 30—75% by volume of plasticiser and 10—55 percent by volume of filler.
  14. A method according to any one of the preceding claims, wherein the poly(*alpha*-olefin) is polyethylene.
  15. A method according to claim 14, wherein the polyolefin component of the blend comprises 0 to 85% by volume of polyethylene of melt index of 0.1 or greater and 15 to 100% by volume of polyethylene of substantially zero standard load melt index.
  16. A method according to any one of the preceding claims wherein part or all of the filler or plasticiser or both is removed from the cold worked blend by solvent extraction.
  17. A method according to claim 1 substantially as hereinbefore described.
  18. A blend treated by a method claimed in any one of claims 1—17.
  19. A deformed sheet obtained by a method claimed in any one of claims 1—17.
  20. Tape backing, pipe wrappings and heavy

duty film comprising a deformed blend or sheet  
as claimed in claim 18 or 19.

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